4.1 Synthesis of p-Dimethylaminobenzylidene-p'-methoxyaniline (DABPMA)

The procedure followed while synthesizing the compound DABPMA, has been outlined briefly as follows:

Para-dimethylaminobenzaldehyde (DMAB) and Para-methoxyaniline (PMA) were used as the parent compounds for the preparation of the schiff-base, DABPMA. The commercially available powdered sample of DMAB was purchased from E. Merck (India) and was further purified by crystallizing the powdered sample in dilute ethyl alcohol at room temperature. The purified sample of DMAB was obtained in transparent hexagonal crystal form. The crystals were washed in distilled water (distilled three times) and were dried in blowing air. The other parent compound para-methoxyaniline (PMA) was purchased from Thomas Baker and Co. London, and was used without further purification.

2.99 gms of the purified crystalline sample of DMAB and 2.46 gms of PMA were dissolved in sufficient quantity (about
40ml) of absolute ethyl alcohol. The reaction mixture was purified by slow filtration process. The filtrate was then refluxed continuously in a round bottom flask fitted to a leibig condenser through which cold water was circulated using an electrically-controlled water circulator (MK-70). The process of reflux was carried out at a constant temperature of 90°C and was continued for three hours. The completion of the reaction was checked by using thin-layer-chromatography technique (TLC). The sample, after the completion of the reaction, was left untouched for about ten hours. The solid compound (light greenish yellow in colour) was then separated from ethanol containing traces of the unreacted parent compounds. The solid deposit was collected by filtration and was washed well with cold aqueous alcohol. The product was obtained in sufficiently pure form by crystallizing the sample three times from aqueous methanol. The pure sample was preserved in a dessicator.

4.2 Synthesis of Benzylidene-o-hydroxyaniline (BOHA)

The parent compounds ortho-amino-phenol (OAPH) and Benzaldehyde, used for the synthesis of the Schiff-base Benzylidene-o-hydroxyaniline (BOHA) were obtained from Aldrich with 99% purity of OAPH and 99% of Benzaldehyde and were used without further purification. 2.18 gms of ortho-aminophenol and 2.3 gms of benzaldehyde were dissolved in absolute ethyl alcohol and the procedure mentioned in 4.1 was followed except that the
reaction was continued for four hours in this case. The product, after the completion of the reaction was separated from ethyl alcohol, washed with distilled water and then extracted with chloroform. The compound thus obtained, was finally purified by using silica gel column chromatography (120 mesh size). The compound is light yellow in colour.

4.3 Synthesis of Benzylidene-p-nitroaniline (BPNA), p-Dimethylaminobenzylideneaniline (DABA), Benzylidene-m-hydroxyaniline (BMHA), p-methoxybenzylidene-p'-nitroaniline (PMBPNA) and p-Dimethylaminobenzylidene-p'-hydroxyaniline (DABPHA)

Extrapure AR grade p-nitroaniline was obtained from Sisco Research Lab and was used without further purification. The procedure followed for synthesizing the compound BPNA is same as that mentioned in 4.1. The compound was purified by using the method as mentioned in 4.2. The compound is bright yellow in colour.

The compounds DABA, BMHA, PMBPNA and DABPHA were synthesized by using parent compounds:

Aniline was a product of E. Merck (India), m- amino phenol was a product of Aldrich, Benzaldehyde (chlorine free) was a product of Sigma, p-anisaldehyde was a product of Sigma and p-amino phenol was obtained from Aldrich. The other chemicals are the same as mentioned earlier.
4.4 Elemental Analysis of the Synthesized Schiff bases

In order to confirm the formation of the desired compounds and to check the extent of their purity, the elemental analysis of Carbon, Hydrogen and Nitrogen was performed for all the Schiff bases, synthesized for present studies. The elemental analysis was performed by microanalytical technique using Heraeus Elemental Analyzer CHN-O-Rapid. The percentage weight of Carbon, Hydrogen and Nitrogen were obtained and were compared with those of the theoretically estimated values. They were found to be in good agreement.

4.5 $^1$H NMR Spectral Analysis of Schiff bases

$^1$H NMR spectra of the synthesized Schiff bases were recorded by using Varian EM-390 NMR Spectrometer at 90 MHz. The conclusions drawn from the $^1$H NMR spectral studies of the compounds synthesized, were utilised to extend support to the mode of bonding containing H-atoms and to provide confirmatory evidences, in favour of their chemical structures.

4.6 Sample Preparation and Recording of Raman Spectra

The solid samples were dissolved in spectroscopic grade solvents, purified earlier by distillation process, to make a solution of concentration $\sim 10^{-4} \text{M}$. The solutions were purified by slow filtration process. To record the Raman spectra, about 2.3
ml of the prepared solution was taken in a cylindrical cell, which was positioned in a proper mount. The laser at a selected wavelength was made to strike the bottom edge of the cell. The spectrometer was routinely calibrated with known CCl$_4$ line in lower region i.e. 100 - 500 cm$^{-1}$ and with Indene in the higher frequency range i.e. 1300 - 1675 cm$^{-1}$ and some times with known Raman lines of solvents that were being used. Other spectral parameters such as laser power, integrating time, wavenumber increment, slit-width etc. were adjusted from time to time in order to optimise the signal to noise ratio. For weak Raman signals, the spectra were run several times and were averaged with the help of the Datamate.

The cell was cleaned to free it from grease and finger prints as they can cause a considerable increase in the fluorescent background of the spectrum and from air bubbles which increase the scatter of the laser beam.$^2$

The fluorescent background in the Raman spectra was reduced by purifying the samples by the process of recrystallization. The photodecomposition was found to be minimum and was further avoided by using rotating cell technique.$^{3,4}$ This technique also avoids the local heating leading to thermal lens effect.
References


